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A NONMECHANISTIC DESCRIPTION OF SOME CHEMICAL REACTIONS

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INTRODUCTION

The common method of describing reaction kinetics from the mechanistic viewpoint is with the aid of the empirical rate equations. From a consideration of the nature of the reacting species and the rate at which they are consumed, the intermediate steps by which the products are formed can be postulated and the transient species involved identified.

Consider the following chemical reaction that occurs in a closed isothermal system

$$aA + bB + \ldots + mM \rightarrow cC + dD + \ldots + nN \quad (1)$$

From this mechanistic viewpoint, equation (1) illustrates only the stoichiometry of the reaction and does not reveal in any manner the processes by which the products are formed. The order and molecularity of the reaction is divorced from the stoichiometric coefficients.

This reaction may be described in an alternate fashion, not as a dynamic system involving collisions between polyatomic species, but as a series of stationary states at various times. For example, consider two arbitrary states, an initial and a final, at times t_i and t_f. The nonmechanistic description consists of the knowledge of the nature of the initial and the final states and of the time necessary for transformation from one to the

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other to occur, but not the manner in which this process is carried out. Such a nonmechanistic description can be one of classical thermodynamics in which each state has a unique energetic description independent of the manner in which the state was attained.

THERMODYNAMIC CONSIDERATIONS

Consider the free-energy difference between the products and the reactants as defined from classical thermodynamics. This function has a unique value ΔG_i and ΔG_f associated with the initial and final states, respectively. From thermodynamic convention, this free-energy difference must have a negative value for reaction (1) to proceed in the direction illustrated and will increase as the reaction proceeds. Thus $\Delta G_f > \Delta G_i$, and

$$\left[\frac{\partial\,\Delta G}{\partial t}\right]_T > 0. \tag{2}$$

Relationship (2) is as far as classical thermodynamics can be used in describing the kinetic behavior of reaction (1) in terms of the free-energy difference.

Finding a specific solution to the inequality expressed in relationship (2) for a particular reaction will require an empirical approach. This approach will involve expressing the free-energy term of relationships (2) in terms of experimentally measurable quantities and then determining empirically the particular manner in which the value of the free-energy term increases as the reaction proceeds.

The activity quotient Q is an experimentally determinable quantity. By definition

$$Q = \frac{[C]^c[D]^d\ .\ .\ .\ [N]^n}{[A]^a[B]^b.\ .\ .\ [M]^m}, \tag{3}$$

where the quantities in brackets are the activities of the products and the reactants, and the exponents are the stoichiometric coefficients of reaction (1). The activity quotient is related to the free-energy function by the following expression:

$$\Delta G = \Delta G^{o} + RT \ln(Q), \tag{4}$$

where ΔG^{o} is the free-energy difference when all the products and reactants are in their standard states, R the gas constant, and T the absolute temperature. Differentiation of equation (4) with respect to time yields

$$\left[\frac{\partial \Delta G}{\partial t}\right]_{T} = RT \left[\frac{\partial \ln(Q)}{\partial t}\right]_{T} . \tag{5}$$

Relationship (2) can now be expressed in terms of the activity quotient:

$$RT\left[\frac{\partial \ln(Q)}{\partial t}\right]_{T} > 0. \tag{6}$$

This form of the relationship is amenable to empirical analysis.

EMPIRICAL ANALYSIS

Because the activity quotient is defined in terms of the stoichiometry of a particular reaction, the empirical analysis of various reactions in terms of relationship (6) must be restricted to those reactions that can be represented by a single stoichiometric equation. The actual reaction may proceed in multiple steps and involve intermediate species, but the products must appear and the reactant disappear according to the stoichiometry of the overall equation.

While the activity quotient is experimentally measurable, virtually all kinetic data are in terms of partial pressures or concentrations. Thus, the reactions to be analyzed must not only meet the stoichiometry requirements but must occur at low pressures or in dilute solutions so that the partial pressures or concentrations of reacting species approximate their activities.

To determine empirically the particular manner in which the activity quotient term of relationship (6) varies as a reaction proceeds will require the calculation of the activity quotient at various time intervals. The actual kinetic data with which this study was carried out were solicited from investigators whose results had been reported in the literature. The reactions were restricted to processes that occurred in isothermal closed systems.

Since each of the reactions investigated is characterized by its own particular mechanism, it would be logical to expect relationship (6) to have as many solutions as there are processes to be described. This is not the case, however. For more than two-thirds of the reactions investigated, the logarithm of the activity quotient was found to vary linearly with the logarithm or the elapsed time. This correlation can be expressed in terms of relationship (6) as

$$RT\left[\frac{\partial \ln(Q)}{\partial t}\right]_T \propto \frac{1}{t} . \tag{7}$$

The empirical data supplied by the various investigators were placed directly on punch cards, and, with the aid of an IBM 7094 data processing machine, these data were statistically analyzed to determine how well they were correlated by the logarithmic relationship. The three-sigma confidence limits of the determination coefficient were computed for each reaction. For more than two-thirds of the 101 reactions investigated, the lower confidence limit exceeded 95 percent, which indicated a good correlation. One half of the reactions investigated had a lower confidence limit greater than 99 percent, which indicated an excellent correlation of the empirical data according to relationship (7).

The 101 reactions investigated were distributed among those reported to be zero, first, second, third, and fractional orders, as is illustrated by table 1. Two-thirds of the first, second, and third order reactions were well correlated by relationship (7). There were too few zero and fractional order reactions to evaluate the correlation properly.

Relationship (7) is by no means generally applicable to kinetic data since the reactions that showed good correlations were restricted to those in which the overall reaction was homogeneous and stoichiometric, those that occurred at low pressures or in dilute solutions, and those in which competitive reactions were absent.

Relationship (7) can be expressed as an equation by the introduction of a constant of proportionality G_r:

$$RT\left[\frac{\partial \ln(Q)}{\partial t}\right]_T = \frac{G_r}{t} . \tag{8}$$

Integrating yields

$$\ln(Q) = \frac{G_r}{RT} \ln(t) + C, \tag{9}$$

where C is a constant of integration. If a quantity t_1 is defined as the time at which the activity quotient is unity, equation (9) may be expressed as

$$\ln(Q) = \frac{G_r}{RT} \ln \left(\frac{t}{t_1}\right). \tag{10}$$

The computed values of G_r and t_1 are listed in table 2 for a group of the reactions investigated.

GRAPHICAL CORRELATION

Figures 1 to 11 illustrate graphically the high degree of correlation between the activity quotient and the elapsed time (see equation (9)) for some of the reactions listed in table 2. Figures 1 to 4 illustrate gas-phase reactions, while figures 5 to 11 illustrate liquid-phase reactions. The first three liquid-phase reactions occur in aqueous solutions, the last four in nonaqueous ones. In most cases, the first 60 percent of each reaction was observed, in no case less than 20 percent.

Figures 1 and 2 illustrate the thermal decomposition of four organic compounds. The correlation between the activity quotient and the elapsed time is reasonably good for these reactions, although some deviations were observed, most easily noticed in the case of the decomposition of acetaldehyde. Similar deviations from linearity were found for other organic decomposition reactions in which small amounts of hydrogen, carbon oxides, or simple hydrocarbons were found with the primary products. This indicates a nonstoichiometric reaction.

The decomposition of hydrogen peroxide vapor, shown in figure 3, shows a high degree of correlation at the five temperatures of observation.

The correlation in figure 4 is not as good as that shown by the other gas-phase reactions, but it is comparable with the half-order kinetics used by the experimental investigator.[5] The reaction is heterogeneous. It was reported that the reaction might have been initially inhibited. This may explain the low values for the first data points.

Figure 5 illustrates an electron-transfer reaction in perchloric acid solution. The correlation was quite good at the five temperatures at which this second-order reaction was observed. Other electron-transfer reactions in perchloric acid solutions also show good correlations.

Figure 6 illustrates an ionic reaction in aqueous solution at four temperatures. As in the case of the electron-transfer reactions, the correlation is quite good.

The reaction between ferricyanide and 2-mercaptoethanol in aqueous solution does not show as good a correlation as do the other reactions in aqueous solution, but the data points are somewhat erratic, as shown in figure 7.

The correlation between the activity quotient and the elapsed time is generally quite good for reactions in nonaqueous solutions. The reaction of cis-2-butene episulphide with triphenylphosphine in three organic solvents shows a very high degree of correlation, as illustrated in figure 8. The reactions illustrated in figures 9 and 10 occur in dioxane and ethanol, respectively, and also show good correlations.

Figure 11 shows the reaction of styrene with iodine in carbon tetrachloride to have a considerable deviation from linearity. The initial kinetics were reported as three-halves order in styrene and first order in iodine.[13]

DISCUSSION

This investigation shows that, for many types of homogeneous reactions in which the overall chemical reaction can be specified, the activity quotient varies with time in a describable manner. This nonmechanistic approach is not a generalization, however, because the reactions to which it is applicable are quite restricted. The major condition that must be met is that of stoichiometry. Some of the older data reported in the literature as stoichiometric did not correlate very well. The extreme importance of stoichiometry became evident when some of this data was found to be nonstoichiometric by more recent work.

Although this nonmechanistic approach does not reveal the processes that occur, it does permit some insight into the energetics of the reactions correlated. Specifically, the rate at which the free-energy function increases with time can be found for reactions whose kinetic behavior is adequately described by relationship (7). The addition of equations (5) and (8) yields, after multiplication through by t,

$$\left[\frac{\partial \Delta G}{\partial \ln(t)}\right]_T = G_r \, . \tag{11}$$

Equation (11) can be considered an energetic description (in terms of the free-energy difference) of the stoichiometric reactions described by relationship (7). Equation (11) meets the requirements of classical thermodynamics as expressed in relationship (2) for all the reactions observed; that is, $G_r/t > 0$.

The actual manner in which the free-energy difference varies as the described reactions proceed can be determined by eliminating $\ln(Q)$ between equations (4) and (10):

$$\Delta G = \Delta G^o + G_r \ln\left(\frac{t}{t_1}\right). \tag{12}$$

This equation cannot be valid, of course, for positive values of ΔG. Moreover, one should be cautious of any extreme extrapolation of the data beyond the period of observation.

CONCLUSION

A nonmechanistic description of various reactions has been presented; which permits some insights into the energetics of the reactions. For the reactions that have met the specified conditions (in particular, stoichiometry), this empirical approach has permitted the correlation of the kinetic data with an accuracy at least equal to that attainable with the classic empirical rate equations. In most cases 60 percent or more of each reaction was observed.

ACKNOWLEDGEMENTS

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TABLE 1. - DISTRIBUTION OF 101 REACTIONS INVESTIGATED AMONG VARIOUS ORDERS

Correlation	Order					Total
	0	1	2	3	Fractional	
Good(>95%)	1	26	35	8	0	70
Poor(<95%)	1	8	16	3	3	31

TABLE 2. - VALUE OF PARAMETERS G_r AND t_1 ASSOCIATED WITH VARIOUS CHEMICAL REACTIONS UNDER CONDITIONS CITED

Reaction investigated	Solvent or diluent	Initial concentration, molarity; or pressure, mm Hg	Reaction order	Temperature, °K	G_r, cal/mole	t_1, sec	Ref.
1. Decomposition of di-t-butyl peroxide $(Ch_3)_3COOC(Ch_3)_3 \rightarrow 2(Ch_3)_2CO + C_2H_6$	None	173.5	1	428	2420	103	1
2. Decomposition of dimethyl ether $(CH_3)O \rightarrow CH_4 + H_2 + CO$	None	312	1	777	4430	1520	2
3. Decomposition of acetaldehyde $CH_3CHO \rightarrow CH_4 + CO$	None	363	2	791	2520	452	3
4. Decomposition of azo-isopropane $C_3H_7NNC_3H_7 \rightarrow N_2 + C_6H_{14}$	None	35.15	1	543	2250	1990	4
5. Decomposition of silver oxide $2Ag_2O \rightarrow 4Ag + O_2$	None	0	0.5	623	1870	47.6×10^4	5
6. Reduction of Pu(IV) by Fe(II) in perchloric acid solution Pu(IV) + Fe(II) → Pu(III) + Fe(III)	0.5M $HClO_4$	0.001148M + 0.001167M	2	293.4	1190	17.3	6
	0.5M $HClO_4$	0.001148M + 0.001166M	2	288.6	1180	29.8	
	0.5M $HClO_4$	0.001148M + 0.001167M	2	283.4	1150	50.5	
	0.5M $HClO_4$	0.001149M + 0.001168M	2	279.4	1120	86.4	

TABLE 2. - Continued. VALUE OF PARAMETERS G_r AND t_1 ASSOCIATED WITH VARIOUS CHEMICAL REACTIONS UNDER CONDITIONS CITED

Reaction investigated	Solvent or diluent	Initial concentration, molarity; or pressure, mm Hg	Reaction order	Temperature, °K	G_r, cal/mole	t_1, sec	Ref.
6. Reduction of Pu(IV) by Fe(II) in perchloric acid solution Pu(IV) + Fe(II) → Pu(III) + Fe(III)	0.5M $HClO_4$	0.001140M + 0.001156M	2	275.7	1100	142	6
7. Reaction of sodium cyanide with methyl iodide in aqueous solution $CN^- + CH_3I \rightarrow I^- + CH_3CN$	Water	0.063M + 0.0334M	2	319.3	1290	51.1×10^2	7
	Water	0.063M + 0.0342M	2	304.2	1240	19.7×10^3	
	Water	0.063M + 0.0254M	2	293.7	1160	82.5×10^3	
	Water	0.055M + 0.0266M	2	284.6	1140	26.3×10^4	
8. Reaction of sodium cyanide with tris-(1,10-phenanthroline)-Fe(II) $2CN + Fe(Phen)_3(II) \rightarrow Phen + Fe(Phen)_2(CN)_2$	Water	0.105M + 0.0000313M	2	298	1530	72.0×10^2	8
	Water	0.105M + 0.0000313M	2	283	1200	12.6×10^5	
	Water	0.239M + 0.0000313M	2	298	1680	77.1×10^2	
	Water	0.239M + 0.0000313M	2	283	1250	97.0×10^4	
9. Reaction of ferricyanide with 2 mercaptoethanol in aqueous solution $2Fe(CN)_6^{3-} + 2ESH \rightarrow 2Fe(CN)_6^{4-}$	Water	0.0011M + 0.0189M	2	273	962	45.7×10^6	9
	Water	0.0012M + 0.0206M	2	273	992	18.4×10^6	
10. Reaction of cis-2-butene episulphide with triphenylphosphine $CH_3HCSCHCH_3 + (C_6H_5)_3P \rightarrow CH_3HCCHCH_3 + (C_6H_5)_3PS$	m-xylene	0.314M + 0.314M	2	313	1240	15.5×10^4	10
	N,N-dimethylformamide	0.308M + 0.308M	2	313	1230	11.0×10^4	
	Cyclohexanone	0.301+ + 0.301M	2	313	1250	15.0×10^4	

TABLE 2. - Concluded. VALUE OF PARAMETERS G_r AND t_1 ASSOCIATED WITH VARIOUS

CHEMICAL REACTIONS UNDER CONDITIONS CITED

Reaction investigated	Solvent or diluent	Initial concentration, molarity; or pressure, mm Hg	Reaction order	Temperature, °K	G_r, cal/mole	t_1, sec	Ref.
11. Decomposition of trans-dimeric methyl nitroso $(CH_3NO)_2 \rightarrow 2CH_3NO$	Ethanol Ethanol	0.0000361M 0.0000361M	1 1	338 333	1380 1270	56.9×10^4 15.4×10^5	11
12. Reaction of bis-p-chlorophenylmercury with mercuric iodide $Hg(ClC_6H_4)_2 + HgI_2 \rightarrow 2(ClC_6H_4)HgI$	Dioxane Dioxane	0.001M + 0.001M 0.001M + 0.001M	2 2	318 308	1380 1360	26.8×10^2 41.2×10^4	12
13. Reaction of bis-p-fluorophenylmercury with mercuric iodide $Hg(FC_6H_4)_2 + HgI_2 \rightarrow 2(FC_6H_4)HgI$	Dioxane Dioxane	0.001M + 0.001M 0.001M + 0.001M	2 2	318 308	1290 1280	728 1440	12
14. Reaction of styrene with iodine in carbon tetrachloride $C_6H_5CHCH_2 + I_2 \rightarrow C_6H_5CHI_2CH_2$	CCl_4 CCl_4	0.3472M + 0.000530M 0.3472M + 0.000203M		295 295	320 460	318 133	13
15. Decomposition of hydrogen peroxide vapor with 83.3 mole percent helium $2H_2O_2 \rightarrow 2H_2O + O_2$	Helium Helium Helium Helium Helium	9.60 9.60 9.60 9.60 9.60	1 1 1 1 1	741.7 731.6 721.6 712.8 704.7	5300 5020 4900 4590 4490	167 281 389 646 2170	14

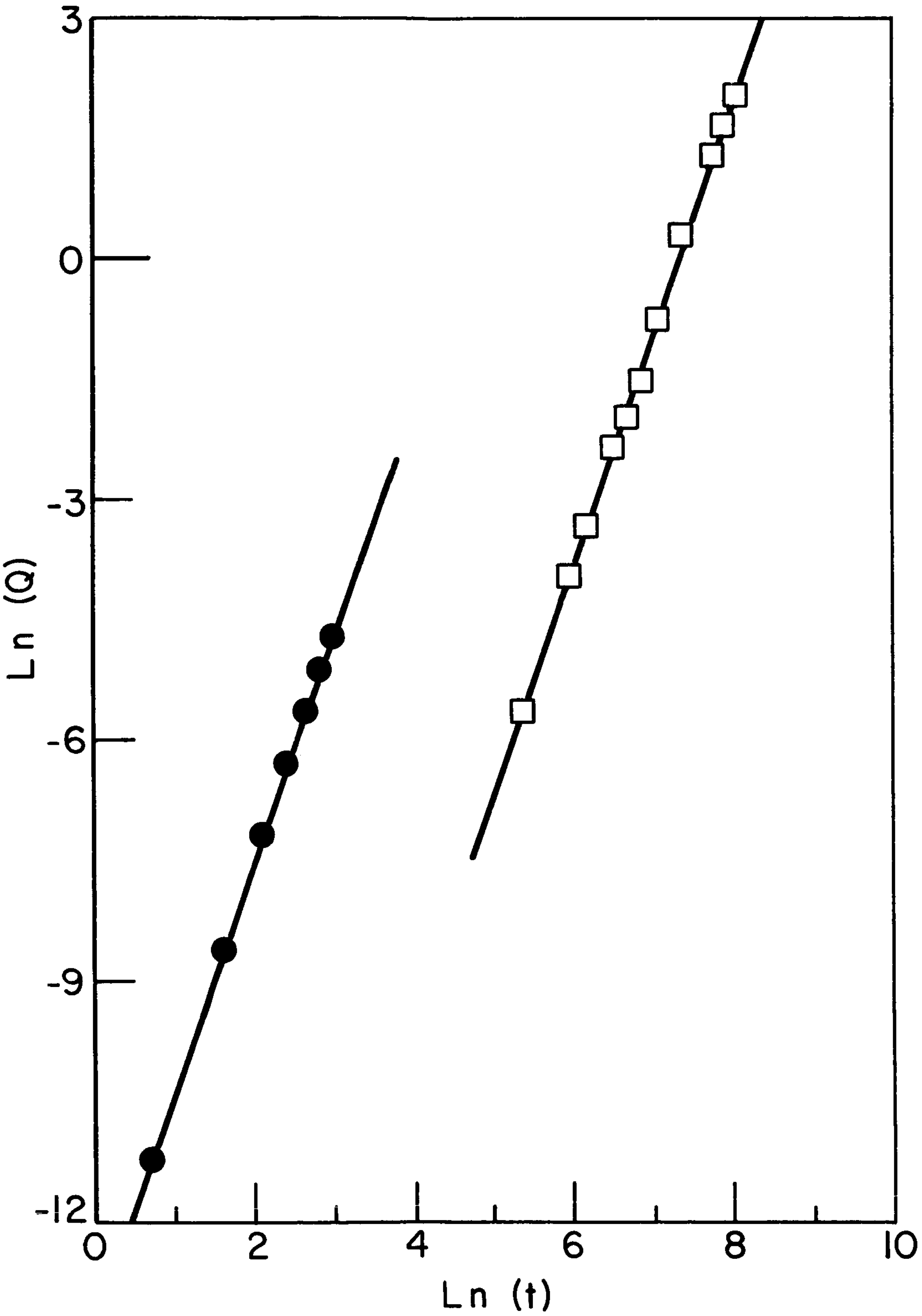

Figure 1. - Decomposition of di-t-butyl peroxide ● (table 2, reaction 1) and dimethyl ether ☐ (table 2, reaction 2).

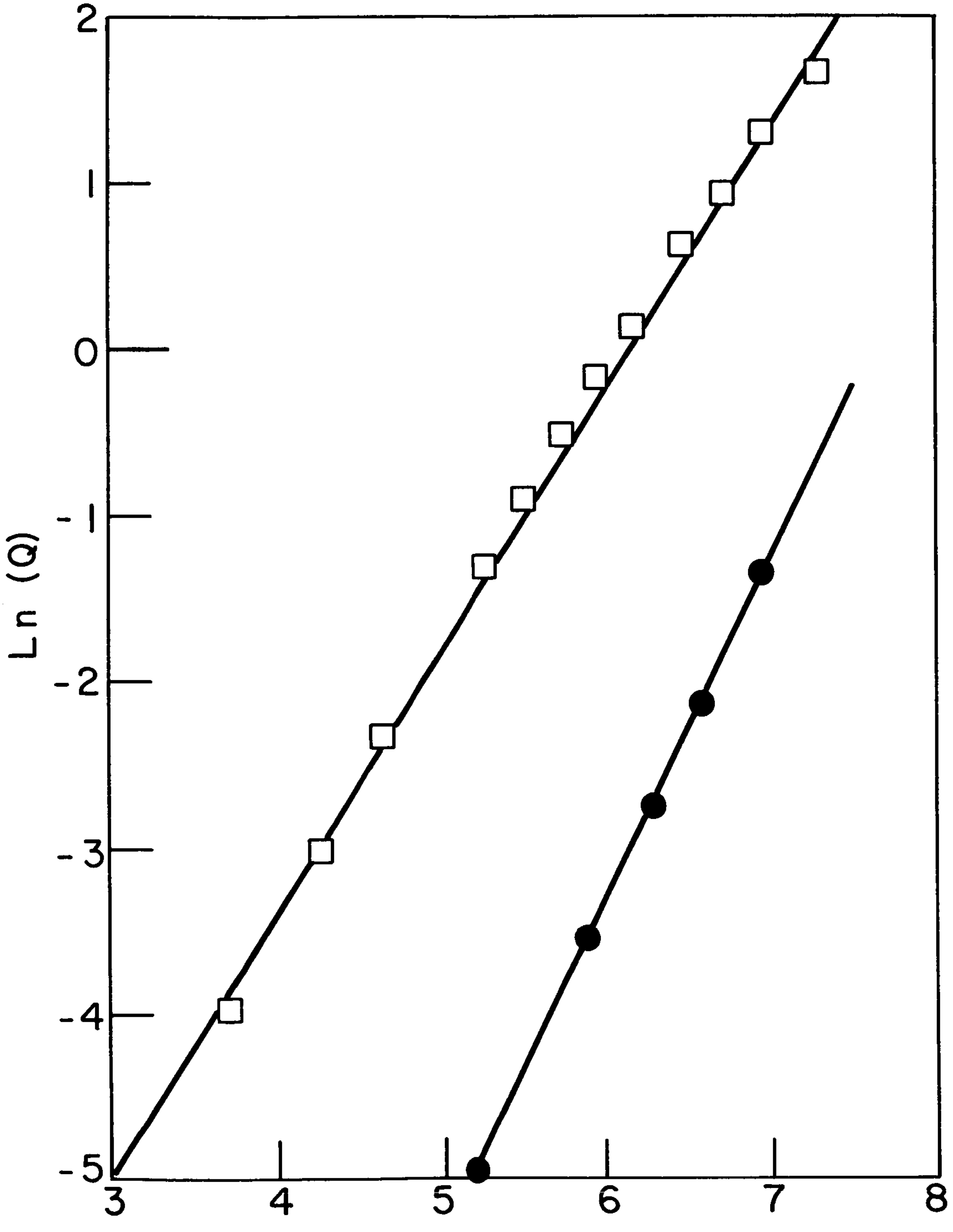

Figure 2. - Decomposition of acetaldehyde □ (table 2, reaction 3) and azo-isopropane ● (table 2, reaction 4).

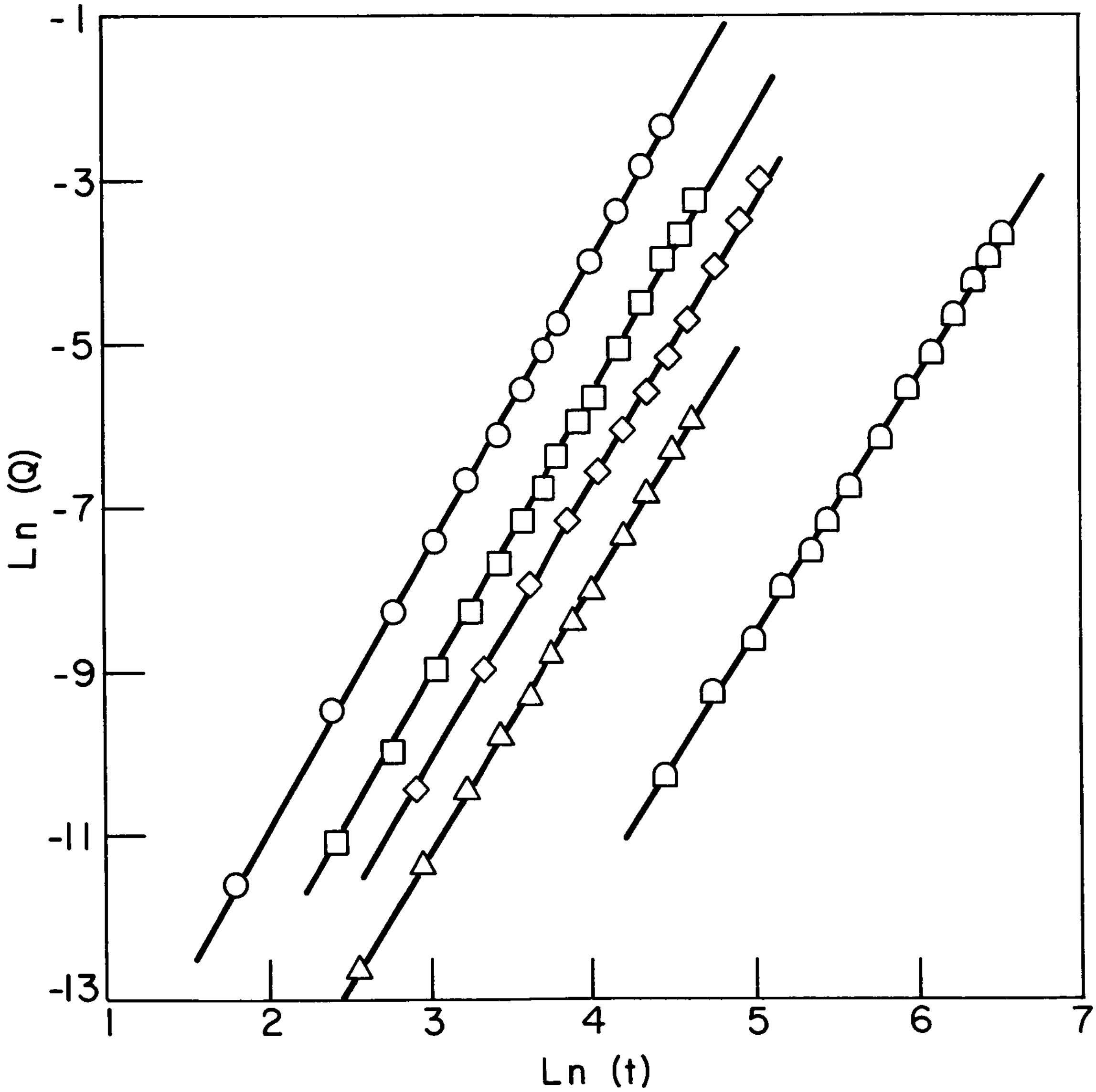

Figure 3. - Decomposition of hydrogen peroxide vapor with 83.3 mole percent helium (table 2, reaction 15). ○ 741.7° K, □ 731.6° K, ◇ 721.6° K, △ 712.8° K, ⌂ 704.7° K.

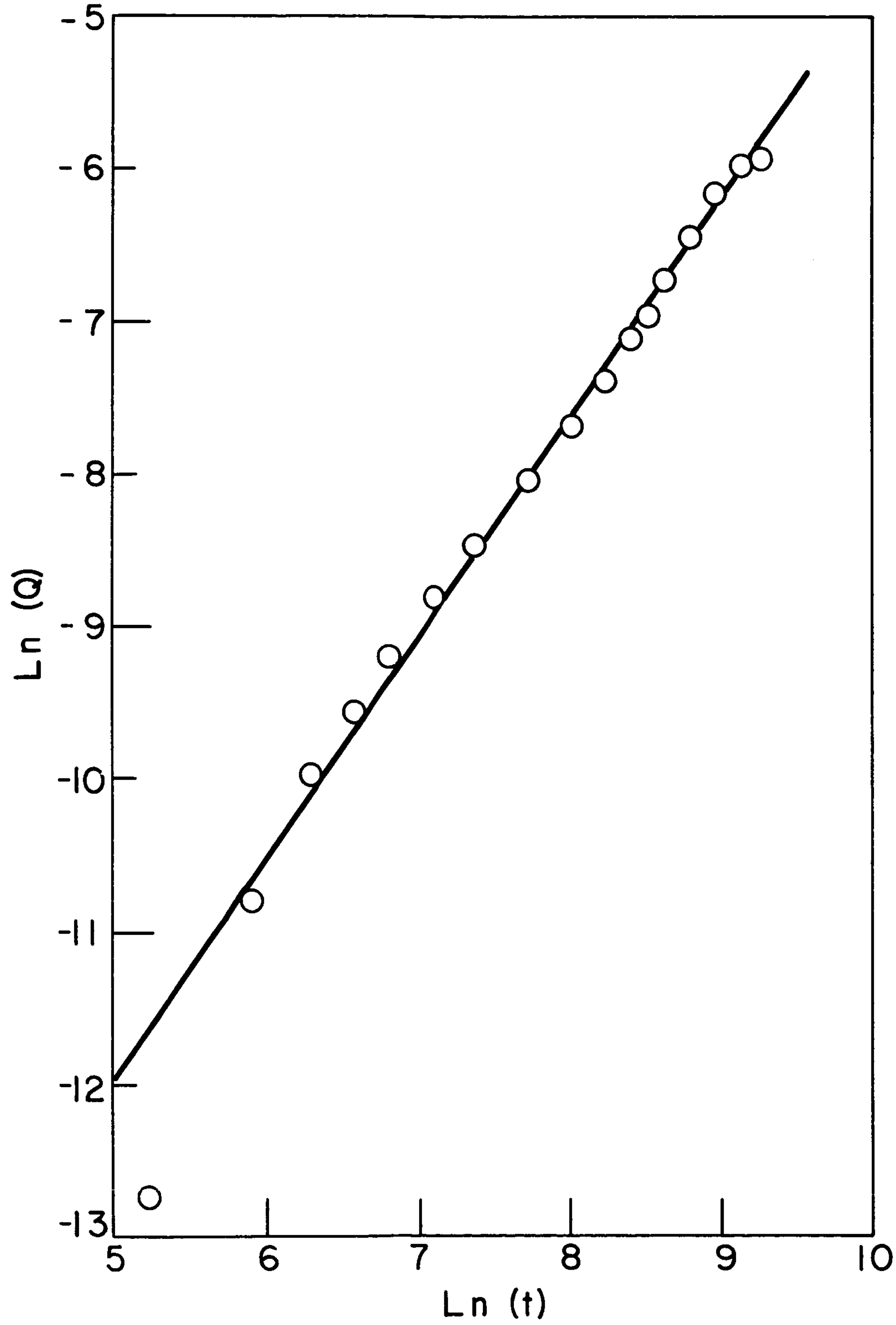

Figure 4. - Decomposition of silver oxide (table 2, reaction 5).

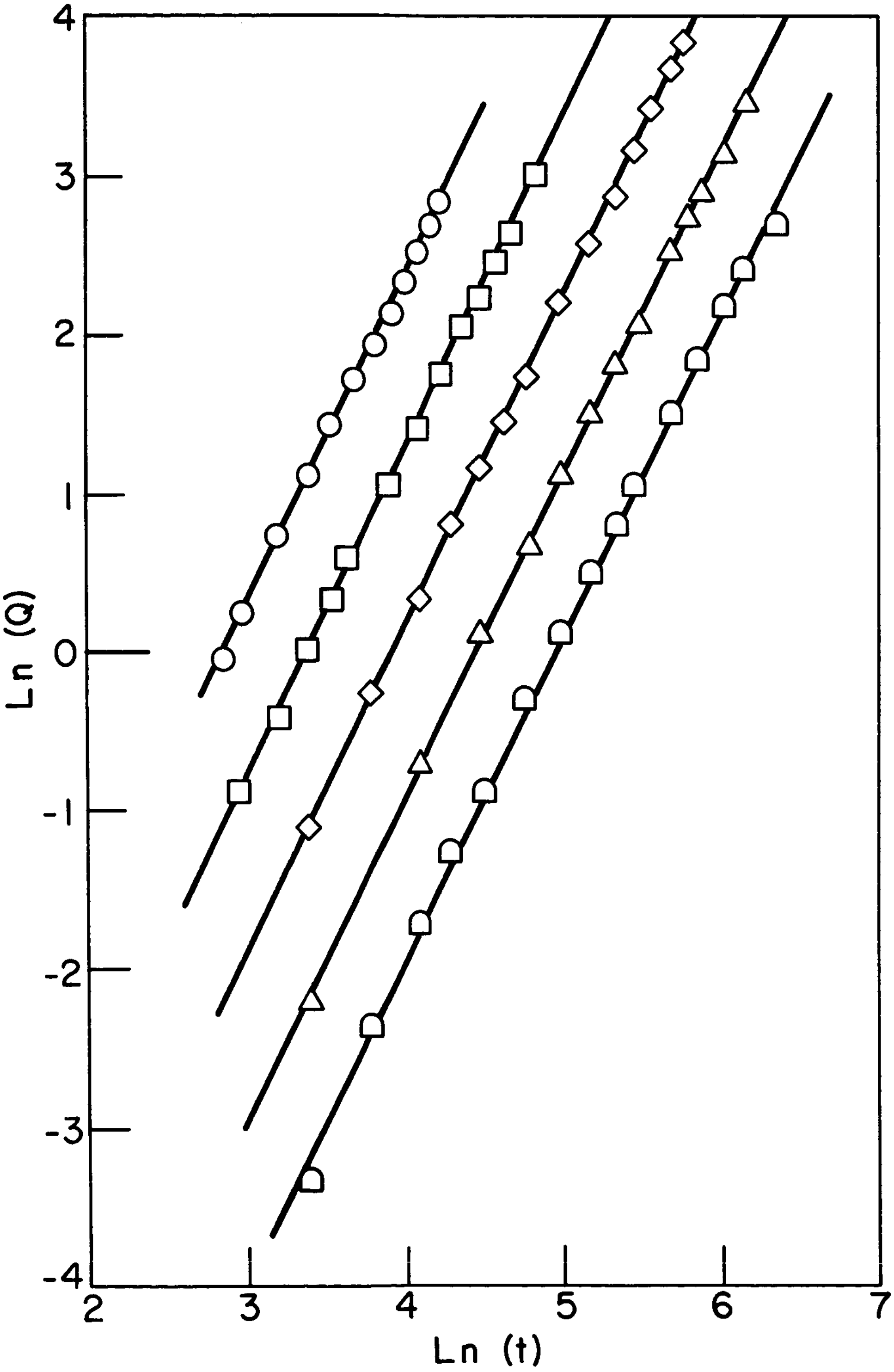

Figure 5. - Reduction of Pu(IV) by Fe(II) in 0.5M perchloric acid solution (table 2, reaction 6). ○ 293.4° K, □ 288.6° K, ◇ 283.4° K, △ 279.4° K, ⌂ 275.7° K.

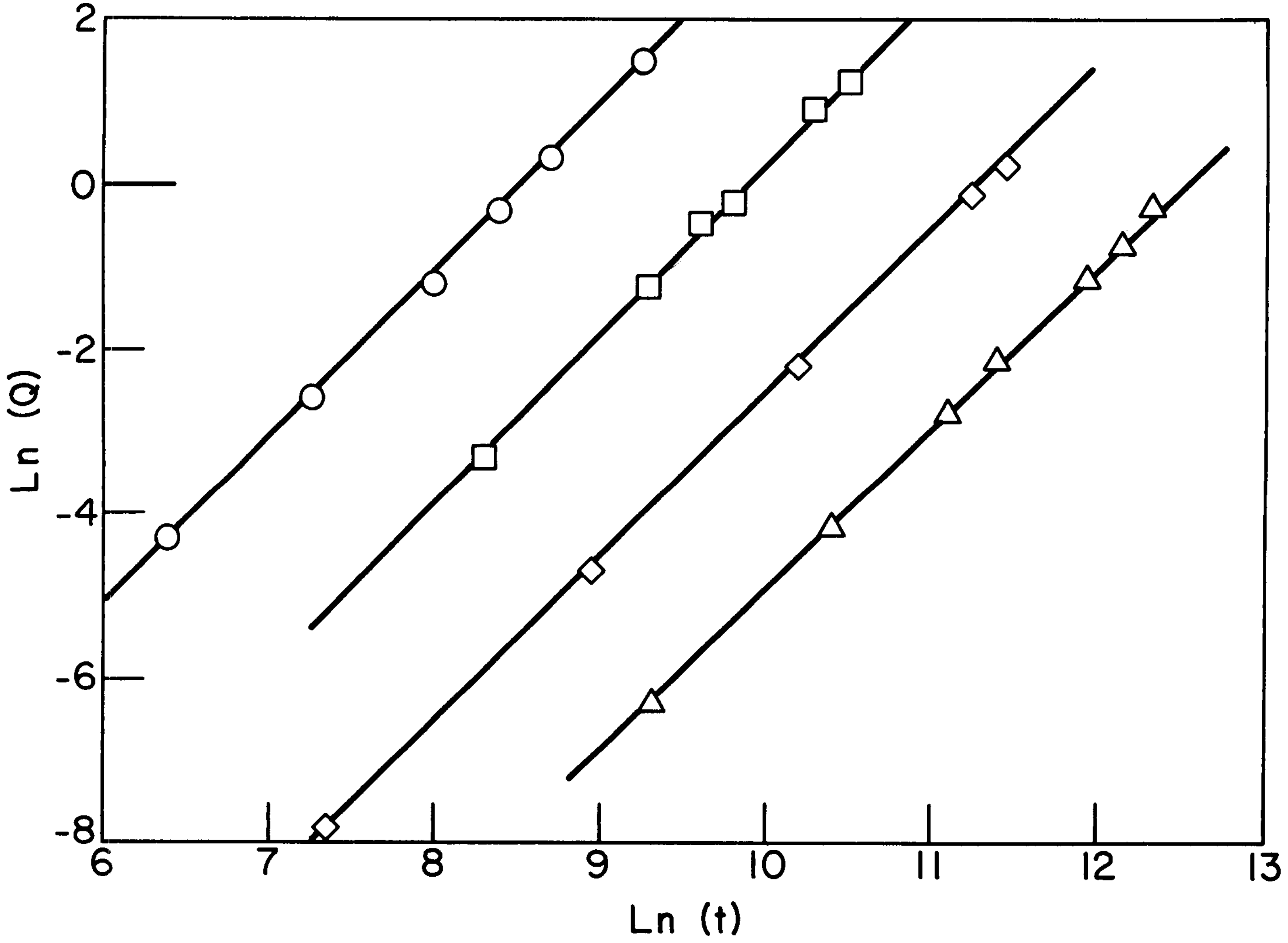

Figure 6. - Reaction of sodium cyanide with methyl iodide in aqueous solution (table 2, reaction 7). ○ 319.3° K, □ 304.2° K, ◇ 293.7° K, △ 284.6° K.

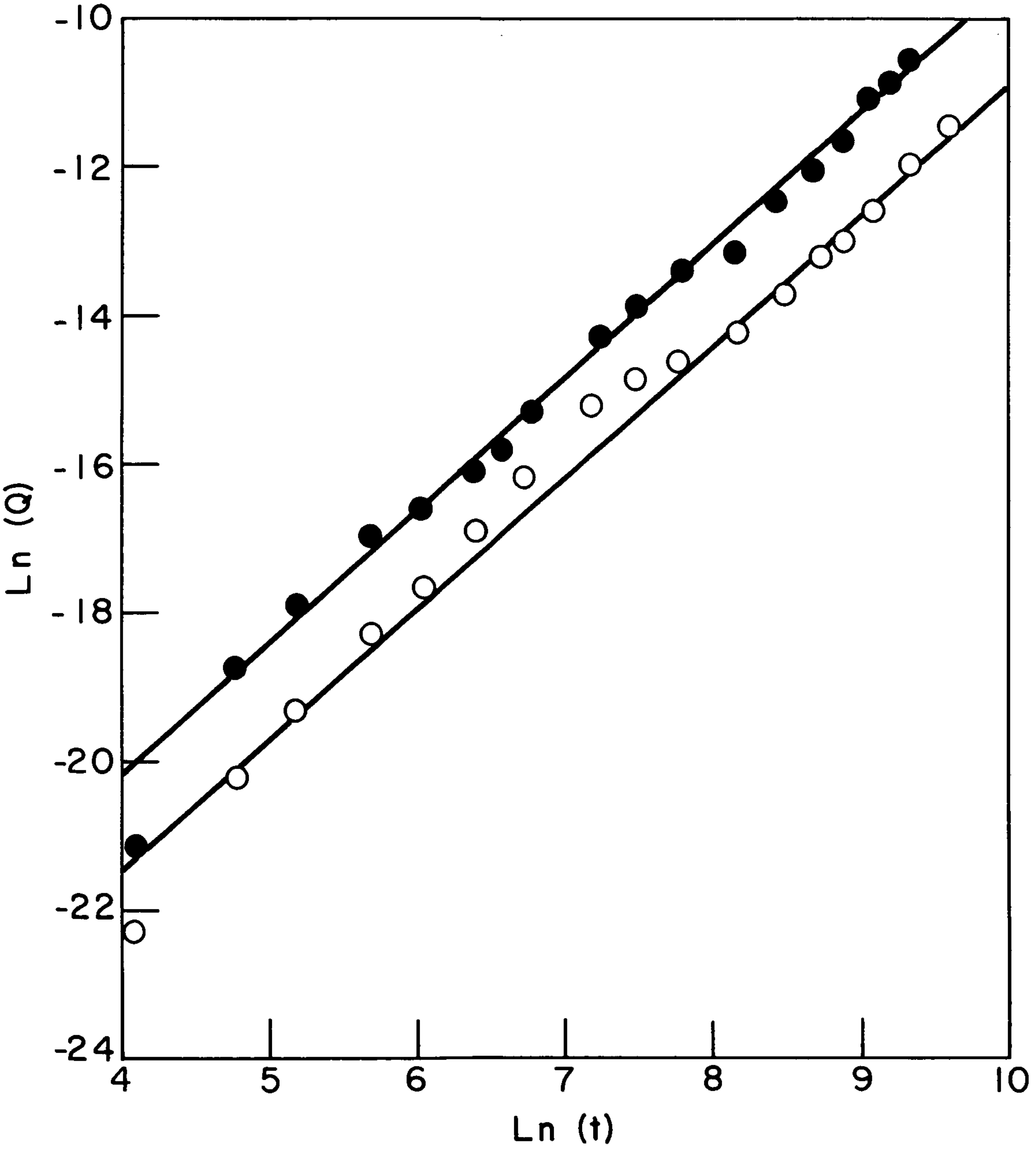

Figure 7. - Reaction between potassium ferricyanide and 2-mercapto-ethanol in aqueous solution (table 2, reaction 9). Initial concentrations - ○ ferricyanide 0.00110M, 2-mercapto-ethanol 0.0189M; ● ferricyanide 0.00119M, 2-mercapto-ethanol 0.0206M.

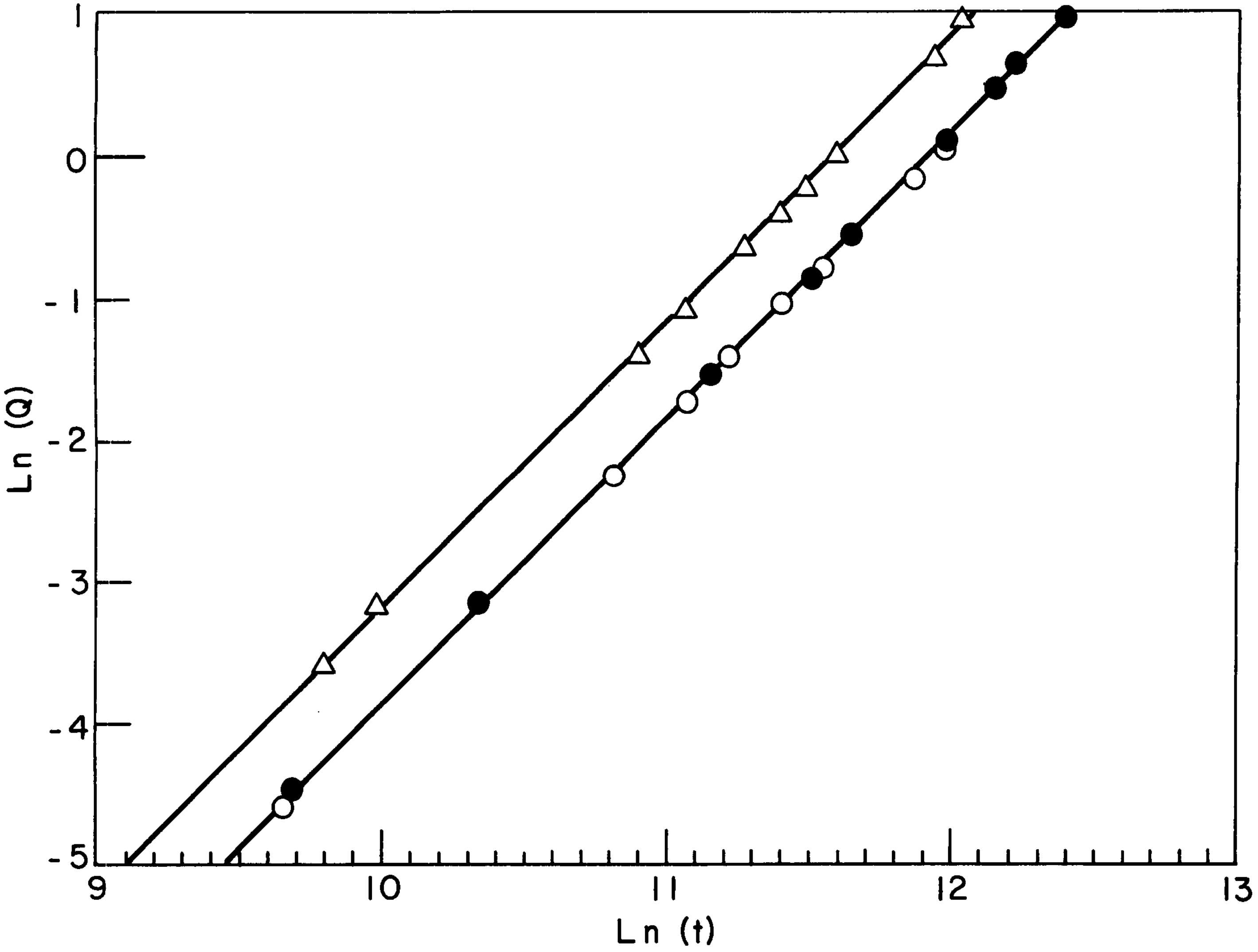

Figure 8. - Reaction of cis-2-butene episulphide with triphenylphosphine in △ N,N-dimethylformamide, ○ m-xylene, and ● cyclohexanone (table 2, reaction 10).

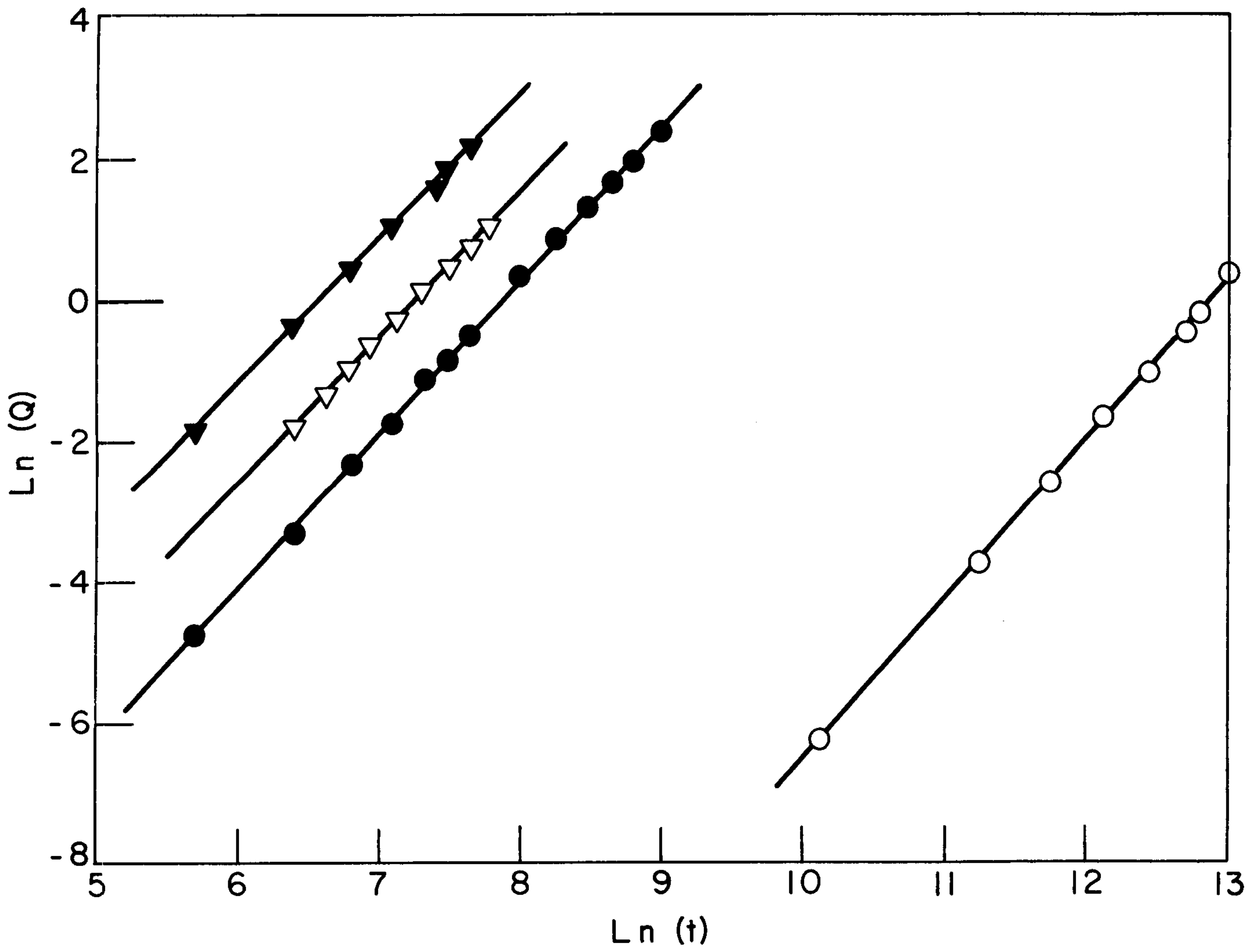

Figure 9. - Reaction of bis-p-chlorophenylmercury (table 2, reaction 12). ● 308° K, ○ 318° K; and bis-p-fluorophenylmercury (table 2, reaction 13). ▼ 308° K, ▽ 318° K, with mercuric iodide in dioxane.

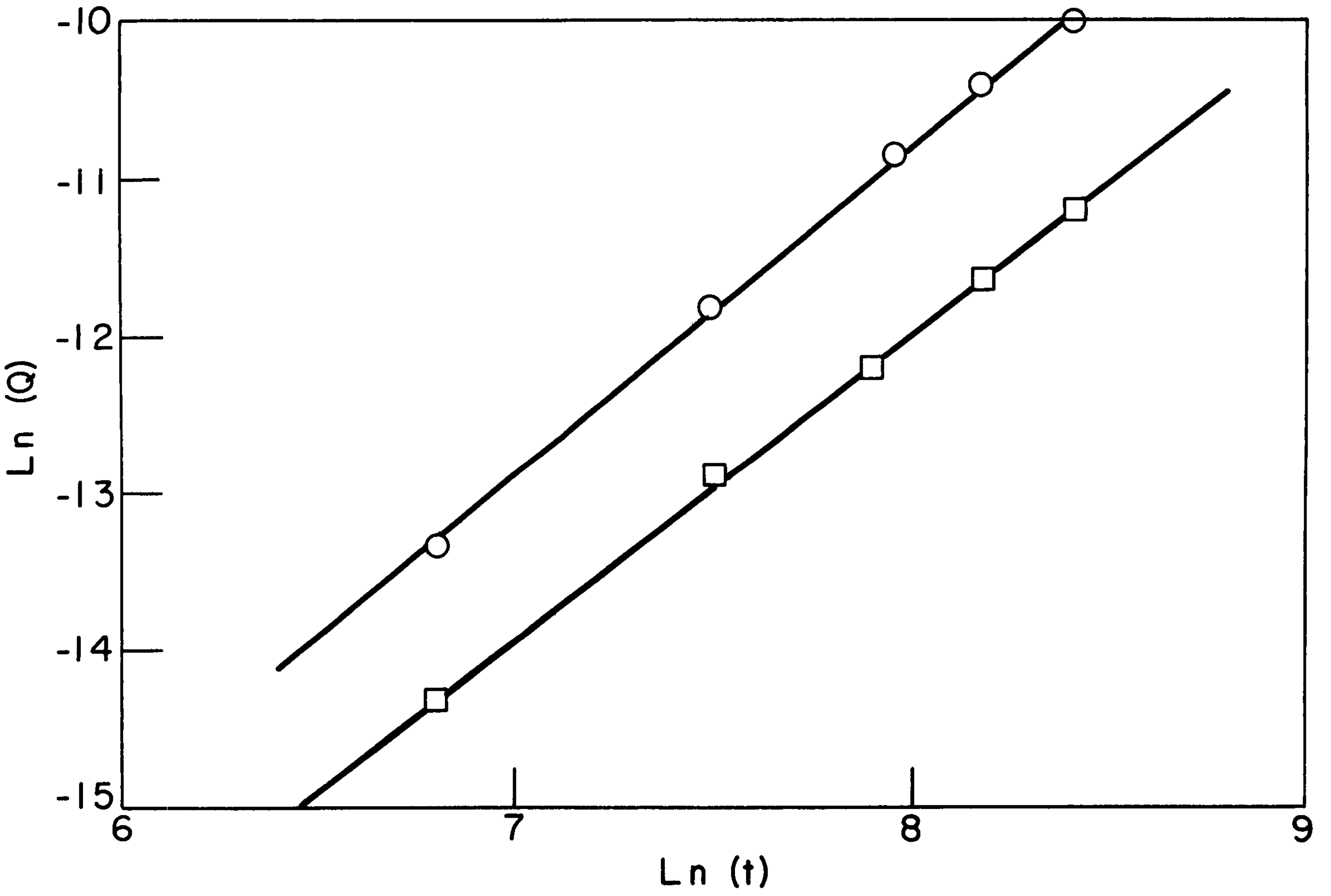

Figure 10. - Decomposition of trans-dimeric methyl nitroso in ethanol (table 2, reaction 11). ○ 338° K, □ 333° K.

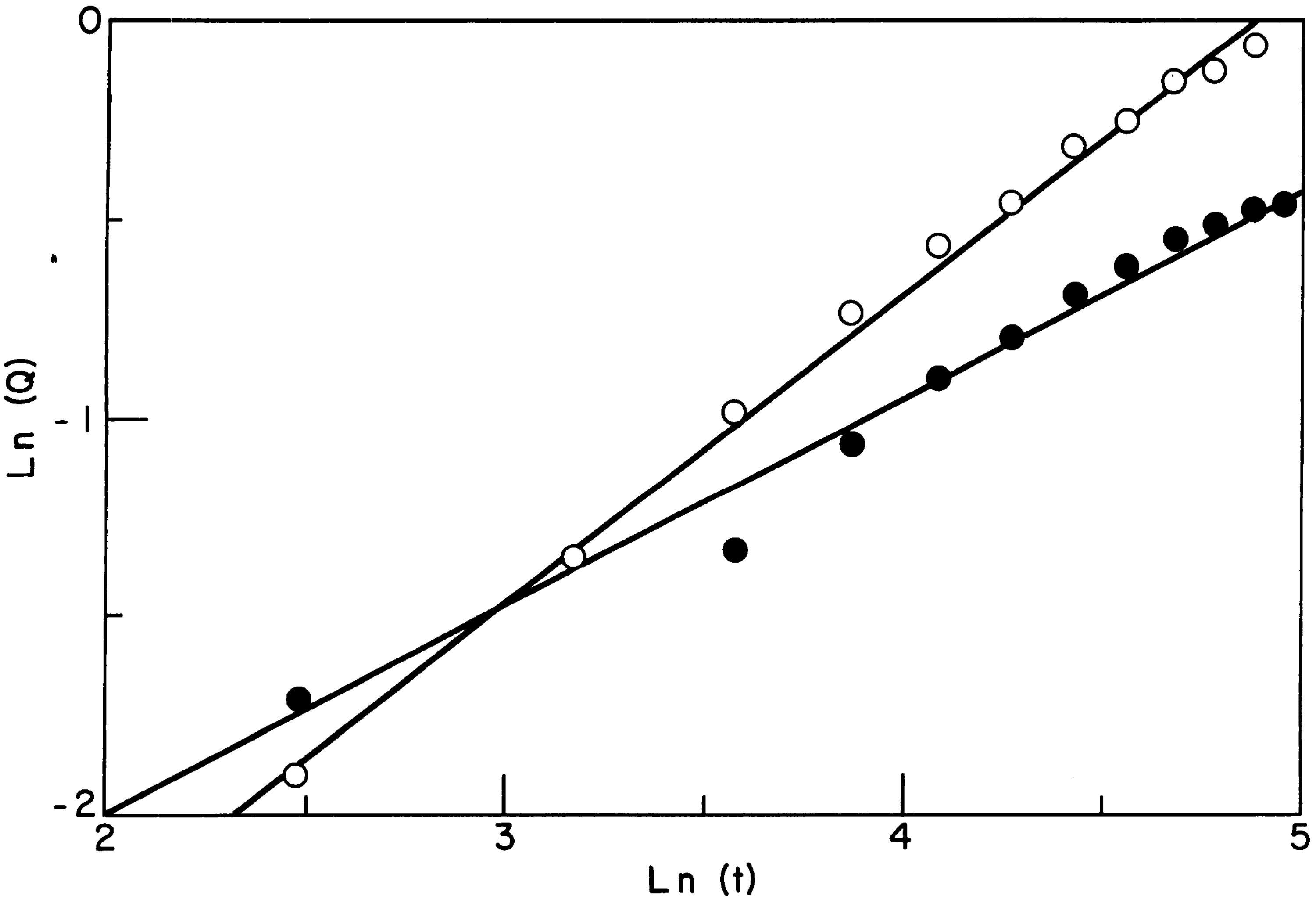

Figure 11. - Reaction of styrene and iodine in carbon tetrachloride (table 2, reaction 14). Initial concentration - ● styrene 0.3472M, iodine 0.00053M; ○ styrene 0.3472M, iodine 0.000203M.